

University of Florida
Development of Novel Water Splitting Catalysts for the Production of Renewable Hydrogen

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Description: This project focuses on the development of iron-based catalysts for the thermochemical splitting of water into hydrogen and oxygen. The thermochemical process of splitting water is particularly well-suited for the utilization of solar energy to provide the heat for the reaction and is a way to produce a renewable hydrogen fuel. As hydrogen is difficult to transport and store, producing hydrogen on site for power plants using proton exchange membrane (PEM) fuel cells or internal combustion engines to generate electricity or for the production of chemicals, such as liquid hydrocarbon fuels, is a very attractive approach. The project uses a two-step process in which water is passed over a reduced iron oxide to generate hydrogen while the oxygen is taken up by the oxygen-deficient iron oxide (Step 1: $\text{FeO}_{x-1} + \text{H}_2\text{O} \rightarrow \text{FeO}_x + \text{H}_2$). In the second step the resulting iron oxide is heated to desorb oxygen and regenerate the oxygen-deficient iron oxide to close the catalytic cycle (Step 2: $\text{FeO}_x \rightarrow \text{FeO}_{x-1} + \frac{1}{2}\text{O}_2$). The main objectives of the project are to develop mixed metal oxide catalysts that 1) will release oxygen at temperatures lower than 1500°C (Step 2), while still maintaining water-splitting activity (Step 1) and 2) are stable up to the temperature necessary for the oxygen desorption step.

Budget: \$ 100,000

Universities: UF

Progress Summary

The high-temperature reactor for testing of water-splitting catalysts has been constructed (Figure 1) and calibrated. An iron oxide catalyst supported on zirconia has been tested in the reactor system and some preliminary data has been collected. Initial results reveal that the catalyst can be regenerated at temperatures of 1,300°C, which is lower than the typical 1,500°C. We are currently working on lowering the temperature further by modifying the catalyst composition.

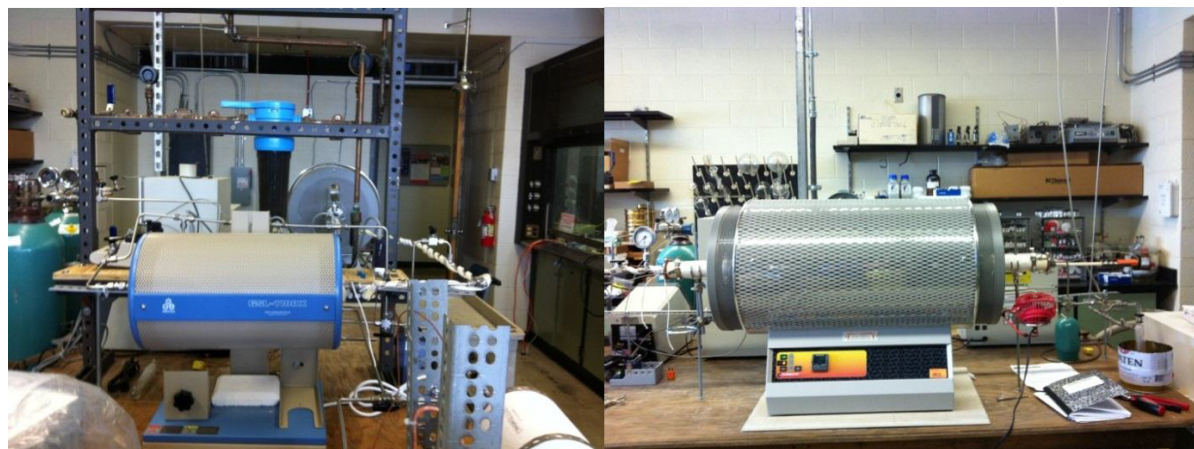
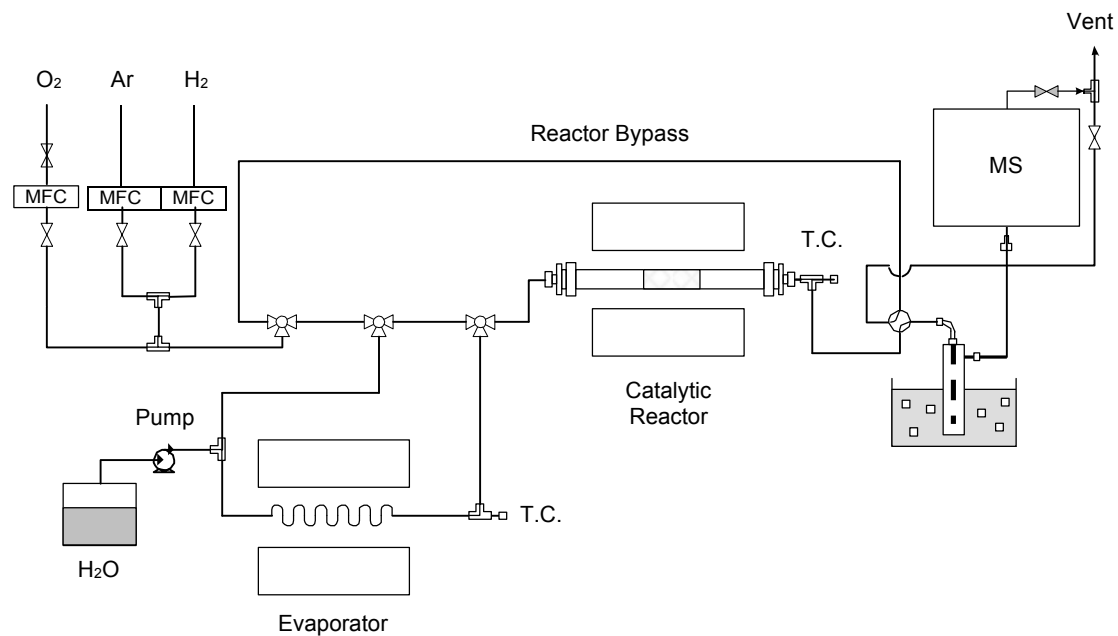


Figure 1. Top: drawing of reactor system. Bottom left: photo of syringe pump and evaporator. Bottom right: photo of high-temperature reactor (mass spectrometer for product analysis is visible in the right hand corner of the photo).

Funds leveraged/new partnerships created

The PI has initiated a collaboration with Dr. Juan Nino in Materials Science and Engineering to design the second generation catalysts. Dr. Nino has extensive experience with solid oxide fuel cell materials, i.e. high-temperature ceramics with oxygen mobility. These materials will be produced as foams by Dr. Nino's group, and the PI will use these as catalysts or catalyst support in the water splitting reaction. Data collected from these foams will be used in future proposals to funding agencies, such as DOE and NSF.

Annual Progress Report

Reactor Construction and Calibration. The reactor system for water splitting has been constructed and calibrated. Figure 1 presents a drawing of the reactor configuration and Figure 2a is a photograph of the assembled system. The reactor system has two modes of operation. The first step is water decomposition, where water (steam) is decomposed over an oxygen-deficient iron oxide catalyst to produce hydrogen and iron oxide. In the second step, the catalyst is heated in a flow of argon until the oxygen desorbes from the iron oxide and the oxygen-deficient iron oxide is regenerated. In both steps the reaction products are monitored on-line using a mass spectrometer.

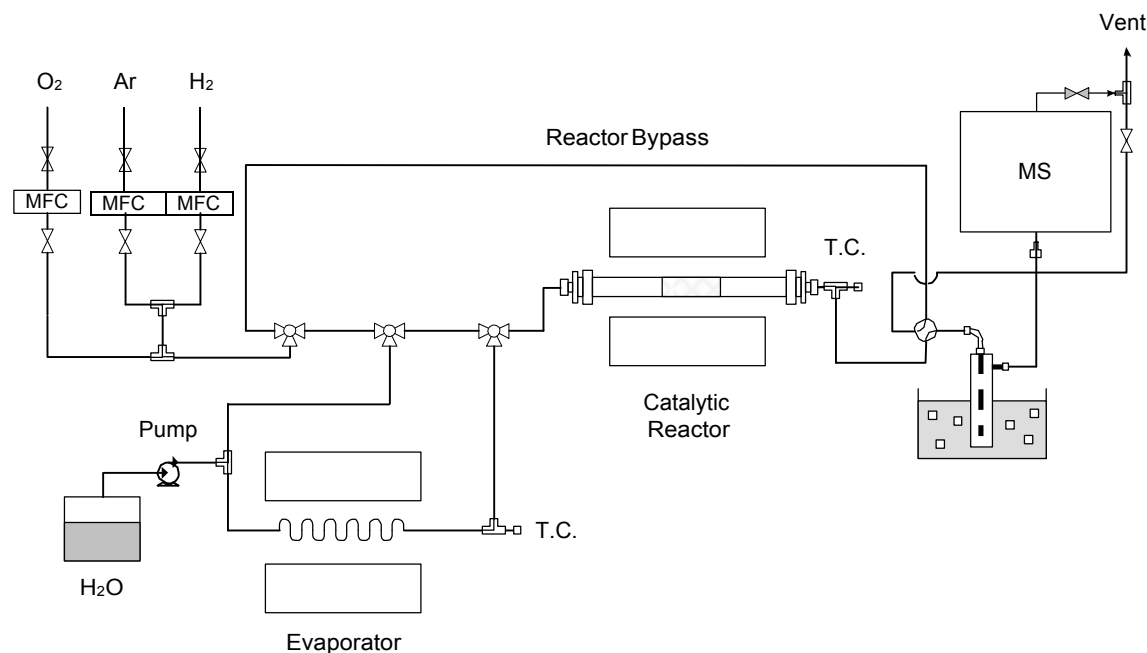


Figure 6: Drawing of The Reactor System For High-Temperature Water-Splitting.

During the water decomposition step, water is pumped into the evaporator using a syringe pump (Figure 2b). Argon is used as the carrier gas for this step, as well as an internal standard for the mass spectrometer and allows quantification of reaction products. The argon is supplied via a mass flow controller, which is displayed in Figure 3a (the figure also includes the mass flow controllers which are used for the calibration of the mass spectrometer). After the evaporator, the lines to the high-temperature furnace, a Carbolite STF 1650 (Figure 3b), are heated to prevent condensation of the steam. The steam then enters the high-temperature furnace, where the catalyst is located. The water in the product stream leaving the reactor is condensed before the gas phase products are analyzed. Steam is continuously introduced until no hydrogen is detected in the products. At this point, the syringe pump and the

evaporator will be bypassed and only argon is fed to the reactor. The temperature in the reactor is then increased until the oxygen desorbs and the catalyst is regenerated.



Figure 2: a) (left) Completed water-splitting reactor system, and b) (right) evaporator furnace used to produce steam for the water-splitting step.

The completed reactor system has been calibrated, which was done by feeding known flow rates of hydrogen and oxygen to the mass spectrometer (MS). In both cases, the argon flow rate was kept constant at the flow rate used during reaction, and the hydrogen and oxygen flow rates were varied. The calibration data is then stored in the MS software and is used to quantify the amounts of hydrogen and oxygen produced during reaction.

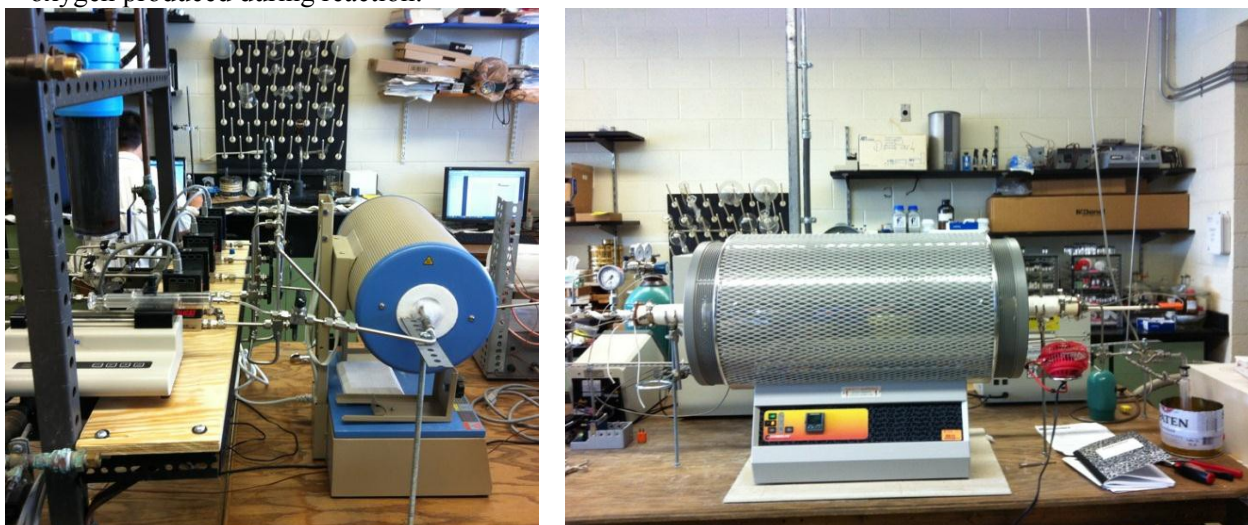


Figure 7: a) (left) the mass flow controllers (MFCs) are the black boxes used to flow argon for the reaction and to calibrate the mass spectrometer. The syringe pump is located in front of the MFCs in the picture and is used to introduce water into the system. The water is evaporated in the furnace to the right of the MFCs and the syringe pump, and b) (right) high temperature furnace.

Activity Measurements. Two catalysts catalysts have been prepared for initial catalyst testing, an iron oxide deposited on zirconia ($\text{FeO}_x/\text{ZrO}_2$) and iron oxide deposited on yttria-stabilized zirconia (FeO_x/YSZ). Initial thermal reduction experiments of the $\text{FeO}_x/\text{ZrO}_2$ have been performed and are shown in Figure 4. In these experiments, the unreduced catalyst ($\text{Fe}_2\text{O}_3/\text{ZrO}_2$) is heated under a flow of argon and the oxygen partial pressure in the reactor outlet is monitored as a function of temperature and time. During these experiments, the catalyst was first heated to 1,000C and the O_2 signal monitored. When no more oxygen could be detected, the reactor temperature was increased in 100°C increments first to 1,100°C and then 1,200°C and so on, while monitoring the O_2 signal. This will continue until 1,500°C, or until no more O_2 is detected in the product stream, whichever comes first. Once a suitable O_2 desorption temperature has been established, this temperature will be used to run several water decomposition and catalyst regeneration (O_2 desorption) cycles.

Future Work. Once data has been collected for the $\text{FeO}_x/\text{ZrO}_2$ and FeO_x/YSZ catalysts, the catalyst compositions will be modified in attempts to increase the hydrogen yield from the water-splitting step and decrease the catalyst regeneration (O_2 desorption) temperature.

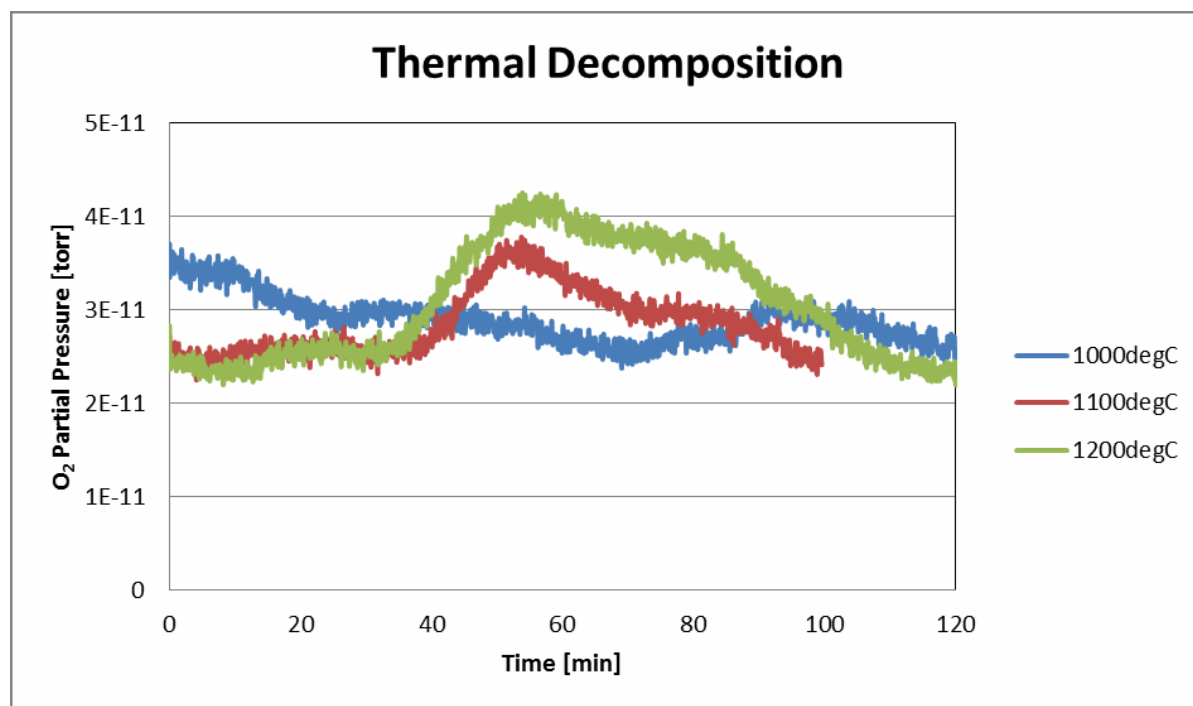


Figure 4: Oxygen evolved during thermal reduction at different temperatures.